Abstract

Surface phenomena such as surface tension and adsorption play important role in various metallurgical and materials applications such as gas adsorption, nucleation and growth of non-metallic inclusions, slag-metal reactions, welding, solidification etc The surface tension driven convection called the Marangoni Convection is an important phenomenon that occurs in welding processes where the weld depth to width ratio is dependent on the surface tension gradient in the weld pool The surface active elements such as oxygen, sulphur etc, greatly influence the surface tension of liquid iron The presence of the surface active species in liquid iron is found to alter the temperature coefficient of surface tension from a negative value to a positive value This results in change in the fluid flow pattern on the surface of the weld pool Hence, the study of the effect of temperature in the systems containing surface active elements is very important in assessing Marangoni Convections normally encountered in the welding processes

The present research concentrates on the Butler's equations to calculate the surface tension and adsorption functions of iron based systems The Butler's equation is given by

$$\sigma = \sigma_i^{\circ} + \frac{RT}{S_i} ln \left(\frac{a_i^m}{a_i} \right)$$

where σ and σ_i° are the surface tension of the alloy and pure species 'i' respectively, S_i is the molar surface area of 'i', a_i^m and a_i are the activities of the species 'i' in the surface and bulk phases respectively Since the alloys of interest have been primarily in the dilute solution ranges, the Butler's equations have been modified by transforming the activities of the solutes into infinite dilute solution as the standard state based on Henrian law These modified Butler's equations have been subsequently used in interpreting the surface tensions of dilute

iron based systems The concept of surface interaction parameters has been introduced in order to interpret the thermodynamic properties of the surface phase of dilute iron based systems Expressions for various first and second order derivatives of surface tension with respect to composition at infinite dilution in terms of the interaction parameters of the surface and those of the bulk phases of dilute ternary systems have been presented A method of deducing the parameters which consists of repeated differentiation of the Butler's equations with subsequent application of the appropriate boundary conditions has been developed The surface tension and adsorption functions of the solutes of the Fe-S-O system have been calculated at 1873 and 1923 K using the Butler's equations in conjunction with the derived values for the surface interaction parameters of the system The calculated values of surface tension and adsorption agree favourably with those of the experimental data for the system at both the temperatures

Further, analysis has been carried out on the thermodynamic behaviour of surfaces and adsorption as a function of temperature and composition in the Fe-S-O systems based on the Butler's equations The calculated values of the surface tensions exhibit an elevation or depression depending on the type of the added solute at a concentration which nearly coincides with that of the other already present in the system Generally, the desorption of the solutes as a function of temperature results in the initial increase followed by a decrease in the values of the surface tension The observations are analysed based on the derived values of the surface interaction parameters in the system

The phenomenon of removal of nitrogen from the iron melts in presence of surface active elements has been extensively studied from the kinetic point of view by several researchers In order to explain this behaviour from the thermodynamics of surfaces, Fe-S, Fe-N and Fe-S-N systems at 1823 K have been studied using the Butler's equations The surface tension and adsorption functions of the solutes have been calculated for these systems using the Butler's equations and the derived values of the surface interaction parameters of the systems The calculated values of the surface tension compare favourably with those of the experimental data of the systems The present analysis indicates similar adsorption behaviour of sulphur for the Fe-S and Fe-S-N systems at 1823 K Although a linear adsorption behaviour is observed in the Fe-N system, an inverse relationship in the adsorption behaviour exists between sulphur and nitrogen in the Fe-S-N system The adsorption behaviour interprets

the observed reduction in the transfer of nitrogen to the melt in presence of the surface active element

As a part of the investigation into the thermodynamics of surfaces and adsorption of dilute iron based systems, experiments were carried out in purified argon atmosphere on the liquid Fe-C-S-O alloys at 1823, 1873 and 1923 K using the Sessile Drop technique The experimental setup includes a high-temperature resistance furnace which uses graphite as the heating element and a Philips BV-26 mobile imaging system to capture the images by means of X-rays A video film of the molten droplets was taken at every temperature of measurement by means of a video hardware/software facility The pictures of the molten drop taken from each video were analysed using a computer program which solves numerically a set of first order ordinary differential equations that describe the sessile drop profile The numerical scheme employed is a combination of the incremental loading technique and the Newton-Raphson method The experimental data indicate lowering of the surface tension values for alloys with low carbon and oxygen contents relative to the corresponding ternary Fe-S-O system for comparable compositions This trend reverses with increase in the oxygen and carbon contents particularly at higher temperatures

In view of the limited experimental data which have been generated in the present investigation, despite non-availability of the bulk quaternary interaction parameter, an attempt has been made to interpret the experimental data of the Fe-C-S-O system at 1823 and 1873 K The necessary binary and ternary parameters of the constituent binary Fe-C, Fe-S and Fe-O and ternary Fe-S-O, Fe-C-S and Fe-C-O systems are assessed from the data available in the literature at 1823 and 1873 K The calculated values of surface tension exhibit good agreement with those of the experimental data for all the constituent binary and ternary systems The bulk quaternary interaction parameter $\Psi(fe)$ is estimated using the 'Central Atoms Model' Using the generated experimental data, the surface interaction parameter $\Psi(m)$ has been estimated and used to calculate the surface tension of the quaternary system via the modified Butler's equations in conjunction with the consistent thermodynamic properties of the quaternary system The calculated surface tension values agree well with those of the experimental data for alloys containing low oxygen contents at 1823 K, but those containing higher oxygen contents depart from the experimental data This is attributed to the non-availability of the bulk quaternary interaction parameter $\Psi(fe)$ and use of the dilute

solution model for the system The comparison between the calculated and experimental data agree within 150 mN/m with those of the experimental data at 1873 K of the system